

BEST AVAILABLE COPY

KIRK-OTHMER

EDITORIAL BOARD

HERMAN F. MARK
Polytechnic Institute of New York

DONALD F. OTHMER
Polytechnic Institute of New York

CHARLES G. OVERBERGER
University of Michigan

GLENN T. SEABORG
University of California, Berkeley

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

THIRD EDITION

VOLUME 21

SILVER AND SILVER ALLOYS
TO
SULFOLANES AND SULFONES

EXECUTIVE EDITOR
MARTIN GRAYSON
ASSOCIATE EDITOR
DAVID ECKROTH

A WILEY-INTERSCIENCE PUBLICATION
John Wiley & Sons
NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

BEST AVAILABLE COPY

492 STARCH

STARCH

Starch [$(\text{C}_6\text{H}_{10}\text{O}_5)_n$], the principal reserve polysaccharide in plants, constitutes a substantial portion of the human diet. It is the principal component of most seeds, tubers, and roots and is produced commercially from corn, wheat, rice, tapioca, potato, sage, and other sources. Most commercial starch is produced from corn which is comparatively cheap and abundant throughout the world. Wheat, potato, and potato starch are produced on a smaller scale and at higher prices.

Nonfood uses of starch have a long history, and Egyptian papyrus cemented with a starchy adhesive has been dated to 3500-4000 BC. Pliny the Elder (130 BC) described the uses of a modified wheat starch in sizing papyrus to produce a smooth surface (see Paper: Papermaking additives). Today, starch is used extensively in the paper, textile, and adhesive industries and has many other applications. Emergence of immobilized-enzyme technology has given rise to the production of sweeteners (qv) from corn starch (ie, corn syrup, high-fructose corn syrup), and work is underway in many laboratories to determine the extent to which cereal grains or their starches can be utilized as sources of chemical feedstocks, replacing nonrenewable petroleum sources (see Chemistry: Enzymes; immobilized).

Starch is a mixture of linear (amylose) and branched (amylopectin) polymers of α -D-glucopyranosyl units. Natural starch occurs usually as granules composed of both linear and branched starch molecules. However, some starches are composed only of branched molecules, and these are termed waxy starches because of the vitreous sheen of a cut seed surface. Some mutant seed varieties have been produced with starches having up to 85% linear molecules, although most starches have ca 25% linear and 75% branched molecules.

The quasi-crystalline granules that characterize starch ultrastructure are insoluble in water at ambient temperature and relatively resistant to carbohydrates other than α -amylases (see also Carbohydrates; Sugar).

Physical Properties

Starch occurs in plants in the form of granules which may vary in diameter from 2-150 μm (1). Rice starch has the smallest granules and potato starch the largest (2). Microscopic examination of starch granules reveals a distinct cleft called the hilum (1). The hilum is the botanical center of the granule, ie, it is the nucleus around which granule growth occurred. Microscopic examination with polarized light reveals a birefringence which, along with x-ray diffraction, is evidence of semicrystallinity of the granule. Between crossed Nicol prisms of the microscope, a black cross, ie, a cross of isoclines, is observed at the center of the hilum. Cereal starches give an A-type x-ray spectrum, tuber starches a B-type pattern, and a few starches give an intermediate diffraction pattern, the C type (3).

Undamaged starch granules are insoluble in cold water but imbibe water reversibly and swell slightly. The percent increase in granule diameter ranges from 9.1% for corn to 22.7% for waxy corn (4). However, in hot water, a larger irreversible swelling occurs producing gelatinization. Gelatinization takes place over a discrete temperature range that depends on starch type.

Vol. 21

STARCH

STARCH 493

	Range, °C
potato	59-68
tapioca	58.5-70
corn	62-72
waxy corn	63-72
wheat	58-64

At a certain temperature in the heating process (the lower limit of the gelatinization temperature), the kinetic energy of the system is sufficient to overcome the hydrogen bonding in the interior of the starch granule. The amorphous regions of the granule are solvated first, and the granule swells rapidly, eventually to many times its original size. During swelling, and as a consequence of it, some of the linear amylose molecules are leached out of the granule into solution. When a cooked starch paste containing amylose molecules, swollen granules, and granule fragments is cooled, the mixture thickens and, if sufficiently concentrated, may form a gel. The property of forming thick pastes or gels is the basis of many starch uses. The gelatinization temperature is the range between the lower limit, indicating onset of granule swelling, and the upper limit, corresponding to the point where almost all granules are 100% gelatinized. The gelatinization range depends upon the method used to measure it. The most sensitive method follows microscopically the loss of birefringence of a starch slurry heated on a Kofler hot stage. Other chemicals present in the slurry may affect the gelatinization range in a predictable way, and this information may be important to certain industrial applications of starch. Certain chemicals, such as sodium sulfate, sucrose, and dextrose, inhibit gelatinization and increase the gelatinization temperature, probably by competing for available water. Other chemicals, such as sodium nitrate, alkali, and urea, lower the gelatinization temperature range, possibly by disrupting granular intermolecular hydrogen bonds.

The physical properties of starch are altered by mechanical treatment. If in the dry state the granular integrity is disrupted, as by grinding, the starch gelatinizes more readily in cold water. Furthermore, the granule is readily attacked by chemicals and enzymes. In the swollen state, the granule is more fragile, and vigorous agitation of a cooked paste results in rupture of most, if not all, granules. Consequently, the cold paste loses its viscosity and gelling ability.

Specific optical rotation values [$\alpha_{\text{D}}^{\text{D}}$] for starches range from 180 to 220° (3); for pure amylose and amylopectin fractions, $[\alpha]_D$ is 200°. Measurements of these values are hampered by the limited solubility of these polymers and the opacity of some of their dispersions. More recently, the structure of amylose has been investigated with infrared spectroscopy (6). Analysis of the spectrum shows it to be consistent with the proposed ground-state conformation of the monomer D-glucopyranosyl units. The nature of intramolecular bonding in amylose has also been investigated with nmr spectroscopy (7).

Chemical Properties

Most common starches contain two different types of D-glucopyranose polymers. Amylose is essentially a linear polymer of α -D-glucopyranosyl units linked (1→4) as shown in Figure 1. This polymer may be separated from the starch by complete gelatinization and vigorous dispersion of the hot starch solution with a complexing agent such as 1-butanol (8) in water. On cooling, an amylose-butanol complex crystallizes

BEST AVAILABLE COPY

Exhibit 14

502 STARCH

fabric finishes (see 'Textiles'). In this application they serve to increase yarn strength and abrasion resistance and generally improve weaving efficiency. Thin-boiling starches also find some applications in paper manufacture and laundry-starch preparations.

Oxidized starches, principally those prepared by hypochlorite oxidation, are mainly used in paper coatings and adhesives to improve surface characteristics for printing or writing. Oxidized starches are also employed as textile warp sizes and finishes, in the manufacture of insulation and wallboard, and in laundry spray starch.

Starch pyrodextrins and British gums have the ability, in aqueous solution, to form films capable of bonding like or unlike materials. As such, they have extensive use as adhesives for envelopes, postage stamps, and other products (see Adhesives). These dextrins are used in glass-fiber sizing, to protect the extruded fiber from abrasion, and as binders for metal core castings, water colors, briquettes, and other composite materials.

Various organic chemicals, e.g., ethanol, isopropyl alcohol, *n*-butanol, acetone, 2,3-butyleneglycol, glycerol, and fumaric acid, are produced from starch by fermentation (74) (see Fermentation). Other polyhydroxy compounds from starch include D-glucose, sorbitol, methyl α -D-glucopyranoside, and glycerol or glycol-D-glucopyranosides.

Food Uses. Unmodified starch is used in food preparations requiring thickening, gelling, or similar properties. Such applications include puddings, salad dressings, pie fillings, and candies. Pre-gelatinized starch is used in a variety of products where thickening is required but cooking is to be avoided, such as instant pudding, pie fillings, and cake frostings.

Acid-modified starches are used for the manufacture of gum candies because they form hot concentrated pastes that gel firmly on cooling. Heat-treated starches are used in food applications to bind and carry flavors and colors. Sweetening agents are made from starch by enzymatic or acid treatment.

Derivatives

Starches, as polyhydroxy compounds, undergo many reactions characteristic of alcohols, including esterification and etherification. Since the D-glucopyranosyl monomers contain, on average, three free hydroxyl groups, the degree of substitution (DS) may be at most three. The more important commercial starch derivatives are very lightly derivatized (DS < 0.1). Such modifications may produce distinct changes in colloidal properties and generally produce polymers with properties useful in a wide variety of applications.

Hydroxymethyl Starch Ethers. Hydroxymethyl starch ethers of low DS (0.05-0.10) have been produced in a number of ways, usually near the end of the wet-milling process on a high solids-starch suspension. The derivative, a modification of ungelatinized starch, is easily filtered and can be produced economically in a fairly pure form (see also Cellulose derivatives).

In the wet-milling process, a 40-50% solids-starch suspension is treated with a Group I or Group II metal hydroxide and ethylene oxide at ca 50°C. A DS of 0.1 is easily obtained, and the product is still conveniently purified by filtration. Higher DS products are obtainable but are more difficult to purify and filter because the derivatized granules swell during washing.

Vol. 21

STARCH 503

Introduction of hydroxymethyl groups at low DS results in marked modification of physical properties. Among them are reduced gelatinization temperature (75), increased rate of granule swelling (76), and lowered tendency of starch pastes to gel and retrograde.

Low DS hydroxymethyl starches are widely used as paper coatings and sizes to improve sheet strength and stiffness. They are also used as paper-coating color adhesives and to increase internal fiber bonding in paper products. Additionally, hydroxymethyl starches are used as textile warp sizes. Hydroxypropyl and other hydroxylalkyl starches are used as additives in salad dressing, pie fillings, and other food thickening applications (see Food additives).

Cationic Starches. The two commercial cationic starches are the tertiary and quaternary aminoalkyl ethers. Tertiary aminoalkyl ethers are prepared by treating a basic starch slurry with a tertiary amine containing a β -halogenated alkyl, 3-chloro-2-hydroxypropyl radical, or a 2,3-epoxypropyl group. Under these conditions, starch ethers are readily formed that contain tertiary amine free bases. Treatment with acid gives the cationic form. Amines that have been used in this reaction include 2-dimethylaminobethyl chloride, 2-diethylaminomethyl chloride, and N-(2,3-epoxypropyl)diethylamine. Commercial preparation of low DS derivatives requires reaction times of 6-12 h at 40-45°C for complete reaction. The product is filtered, washed, and dried.

Cationic starches exhibit decreased gelatinization temperature and increased hot paste viscosity. Pastes remain clear and fluid even at room temperatures and show no tendency to retrograde. This stability is undoubtedly due to repulsion between the cationic starch molecules in dispersion.

Quaternary ammonium alkyl ethers are prepared in similar fashion: an alkaline starch reacts with a quaternary ammonium salt containing a 3-chloro-2-hydroxypropyl or 2,3-epoxypropyl radical. Alternatively, these derivatives may be prepared by simple quaternization of tertiary aminoalkyl ethers by reaction with reagents such as methyl iodide. Sulfonium (77) and phosphonium (78) starch salts have also been prepared and examined.

Quaternary ammonium starches, like the tertiary ammonium derivatives, show decreased gelatinization temperatures, increased paste clarity and viscosity, and reduced tendency to retrograde. Quaternary ammonium starch salts exhibit cold-water swelling at a DS as low as 0.07. Cationic starches are used on paper mainly for fiber and pigment retention. Their application also improves bursting strength and fold endurance. They have been employed as emulsifiers for water-repellent paper sizes. Because of their relatively high costs, cationic starches are not widely used as textile sizes, although they have been employed in ore refining as flocculating agents (qv).

Starch Phosphates. Starch phosphate monoesters may be prepared by heating a dry mixture of starch and acid salts of ortho-, pyro-, or tripolyphosphoric acid at 50-60°C for 1 h. Degree of substitution is generally low (DS < 0.15), but higher DS derivatives can be prepared by increasing the temperature, phosphate salt concentration, and reaction time.

Compared to the unmodified starches, the monophosphate esters have a lower gelatinization temperature and swell in cold water at a DS of 0.07. Like other derivatives, starch phosphates have increased paste viscosity and clarity and decreased set-back or retrogradation. Their properties are similar to those of potato starch, which also contains phosphate groups.

BEST AVAILABLE COPY

Exhibit 14

504 STARCH

Starch monophosphates are very useful in food applications because of their excellent freeze-thaw stability. As thickeners in frozen gravy and frozen cream-pie preparations, they are superior to other starches. A pregelatinized starch phosphate has been developed (79) which is dispersible in cold water for use in instant dessert powders and icings. Nonfood applications include use as core binders for metal molds, in papermaking to improve fold strength and surface characteristics, as a textile size, in aluminum refining from bauxite ores, and as detergent builder.

In contrast to monophosphates, starch phosphate diesters contain ester cross-links between two or more starch chains. The covalent linkage of the starch chains in the granule produces a starch which, compared to the unmodified starch, swells less and is more resistant to heat, agitation, acid, and rupture of swollen granules.

Starch in aqueous suspension may be cross-linked to form diesters with phosphorus oxychloride, phosphorus pentachloride, and thiophosphoryl chloride (80). Cross-linked starches may also be produced by the reaction with trimetaphosphates (81), which require more vigorous conditions than phosphorus oxychloride. Typically, a starch slurry and 2% trimetaphosphate salt react at pH 10-11 and 50°C for 1 h.

Starch phosphate diesters show a significant increase in the stability of the swollen granules. Depending on the degree of derivatization, the hot paste viscosity may be greater or less than that of the parent starch. In contrast to starch phosphate monoesters, the pastes of the diesters do not increase in clarity. Starches with high DS have exceptional stability to high temperatures, low pH, and mechanical agitation. If the degree of cross linking is sufficient, swelling can be completely inhibited, even in boiling water.

Cross-linked starch derivatives are used as thickeners and stabilizers in baby foods, salad dressings, fruit pie filling, and cream-style corn. They are superior to unmodified starches in their ability to keep food in suspension after cooking, increased resistance to gelling and retrogradation, freeze-thaw stability, and lack of syneresis on standing. They are also used to produce high wet-strength paper (80), as ion-exchangers, and metal sequesterants to prevent oxidative rancidity in oils.

Starch Acetates. Starch acetates may be either low DS or high DS. The commercial importance of low DS acetates is based mainly on the stabilization of aqueous polymer soils. Light derivatization of low DS acetate inhibits association of the amylose polymers and the longer outer chains of amylopectin. These properties are important in food applications. More highly derivatized starches (DS 2-3) are useful because of their solubility in organic solvents and ability to form films and fibers.

Low DS starch acetates are produced by treatment of granular starch with acetic acid or preferably acetic anhydride, either alone or in acetic acid, pyridine, or aqueous alkaline solution. Dimethyl sulfoxide has been used as a cosolvent with acetic anhydride to make low DS starch acetates; ketene or vinyl acetate have also been investigated. Commercially, the acetic anhydride-aqueous alkali system is employed at pH 7-11 and room temperature to give a DS of 0.5.

Low DS starch acetates have lower gelatinization temperatures and less tendency to retrograde after pasting and cooling. Gelling may be completely inhibited if the DS is high enough. Low DS starch acetate polymers also form films useful in textile and paper manufacture.

Lightly derivatized starch acetates are used in food because of their clarity and stability. These applications include frozen fruit pies and gravies, baked goods, instant puddings, and pie fillings. Starch acetates are employed in textiles as warp sizes and in paper to improve printability, surface strength, and solvent resistance.

Vol. 21

STARCH 505

High DS starch acetates are prepared by the methods used for low DS acetates, but with longer reaction time. In general, high DS starch acetates and amylopectin acetates give weak and brittle films and fibers. However, amylose tricetate is useful in forming film and fiber. It is soluble in organic solvents such as acetic acid, pyridine, and chloroform. Films of this high DS acetate, cast from chloroform solution, are pliable, lustrous, transparent, and colorless. These properties are useful in packaging material.

BIBLIOGRAPHY

- "Starch" in ECT 1st ed., Vol. 12, pp. 764-778, by R. W. Kerr, Corn Products Refining Company; "Starch" in ECT 2nd ed., Vol. 18, pp. 672-691, by Stanley M. Parmester, Corn Products Company.
- 1. R. W. Kerr in R. W. Kerr, ed., *Chemistry and Industry of Starch*, Academic Press, Inc., New York, 1950, pp. 9-25.
- 2. O. B. Wurzburg in T. E. Purts, ed., *Handbook of Food Additives*, The Chemical Rubber Company, Boca Raton, Fla., Vol. 1, 1973.
- 3. D. French in ref. 1, pp. 157-178.
- 4. N. N. Hellman, T. P. Boesch, and E. H. Melvin, *J. Am. Chem. Soc.*, **74**, 348 (1952).
- 5. T. J. Schoch and E. C. Maywald in R. L. Whistler and E. F. Paschall, eds., *Starch: Chemistry and Technology*, Vol. II, Academic Press, Inc., New York, 1967, pp. 657-667.
- 6. B. Grau and M. Bergani, *Starch*, **18**, 218 (1966).
- 7. M. S. Jacques, P. R. Sundaramony, J. K. Taylor, and R. H. Marchessault, *J. Am. Chem. Soc.*, **98**, 4386 (1976).
- 8. T. J. Schoch, *Cereal Chem.*, **18**, 121 (1941).
- 9. W. Z. Hassid and R. M. McCready, *J. Am. Chem. Soc.*, **65**, 1157 (1943).
- 10. K. H. Meyer in H. Mark and V. Tobolsky, eds., *Physical Chemistry of High Polymeric Systems*, 2nd ed., Interscience Publishers, Inc., New York, 1950, p. 468.
- 11. C. T. Greenwood, *Starch*, **12**, 159 (1960).
- 12. B. H. Zimm and C. D. Thurner, *J. Am. Chem. Soc.*, **74**, 1111 (1952).
- 13. L. P. Witmeyer, F. R. Seidl, and M. D. Stern, *J. Polym. Sci.*, **16**, 1 (1955).
- 14. G. S. C. Kinchhoff, *Anal. Imp. Sci. Soc. Pittsburgh, Mem.*, **4**, 27 (1911).
- 15. T. deSouza, *Bull. Pharm.*, **6**, 498 (1914).
- 16. G. N. Bathgate and D. J. Mannion, *Biochem. J.*, **101**, 30C (1966).
- 17. E. Y. C. Lee, C. Meister, and W. J. Whelan, *Arch. Biochem. Biophys.*, **125**, 1028 (1968).
- 18. C. Marciel, *Starch*, **25**, 78 (1973).
- 19. J. J. Marshall and W. J. Whelan, *Arch. Biochem. Biophys.*, **161**, 234 (1974).
- 20. J. N. BeMiller in R. L. Whistler and E. F. Paschall, eds., *Starch: Chemistry and Technology*, Vol. I, Academic Press, Inc., New York, 1967, p. 621.
- 21. E. B. Bagley, G. F. Panta, R. C. Burr, W. M. Doane, and C. R. Russell, *Polym. Eng. Sci.*, **17**, 311 (1977).
- 22. U.S. Pat. 3,903,059 (Apr. 3, 1974); U.S. Pat. 3,981,103, 3,985,616, and 3,997,484 (Sept. 8, 1976). M. O. Weaver, E. B. Bagley, E. B. Bagley, G. F. Panta, and W. M. Doane (to United States of America as represented by Secretary of Agriculture).
- 23. B. S. Shasha, W. M. Doane, and C. R. Russell, *J. Polym. Sci. Polym. Lett. Ed.*, **14**, 417 (1976).
- 24. W. M. Doane, B. S. Shasha, and C. R. Russell, *Am. Chem. Soc. Symp. Ser.*, **53**, 74 (1977).
- 25. D. Grabel, *Makromol. Chem.*, **57**, 111 (1963).
- 26. O. L. Brink in G. E. Inglett, ed., *Corn: Culture, Processing, Products*, AVI Publishing Company, Westport, Conn., 1970, pp. 262-291.
- 27. S. A. Watson in ref. 5, pp. 1-51.
- 28. M. J. Wolf, C. L. Busan, M. M. MacMaster, and C. E. Rist, *Cereal Chem.*, **29**, 321 (1952).
- 29. G. Blanchi, P. Arato, and G. Martini, *Cereal Chem.*, **56**, 491 (1979).
- 30. G. C. Shove in ref. 26, pp. 60-72.
- 31. L. T. Fan, H. C. Chen, J. A. Shellenberger, and D. S. Chung, *Cereal Chem.*, **42**, 385 (1965).
- 32. L. T. Fan, P. S. Chu, and J. A. Shellenberger, *Biotechnol. Bioeng.*, **4**, 311 (1962).
- 33. R. A. Anderson, *Cereal Chem.*, **39**, 406 (1962).